SUPPORTING INFORMATION

I. Figures

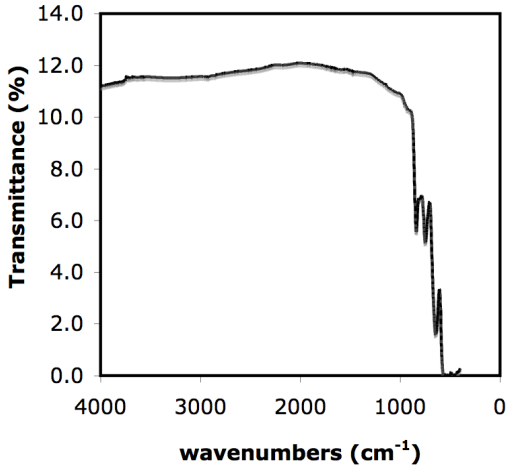

Figure S1. Throughput of GATR setup was 11.8% at 2500 cm^{-1}.

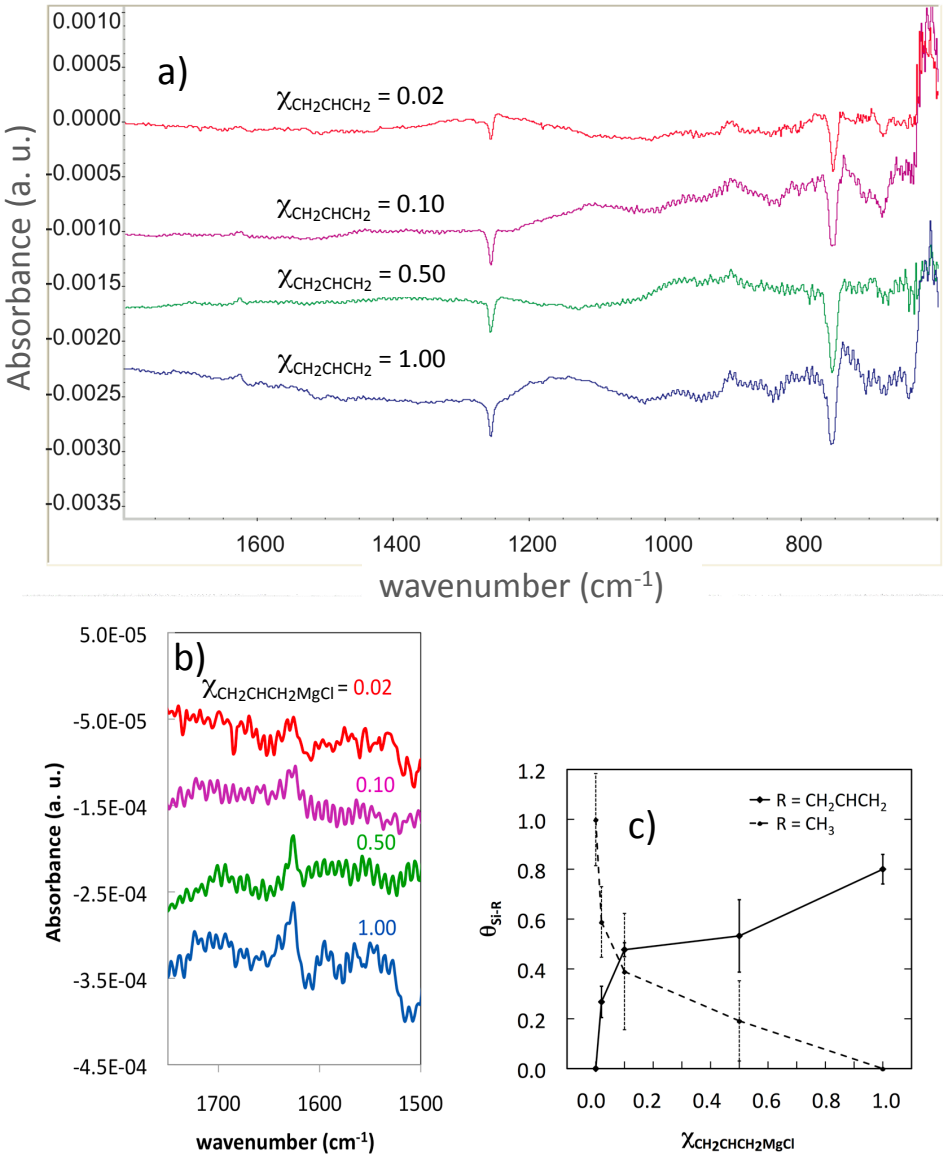

Figure S2. a) Representative transmission spectra of surfaces made with $\chi_{CH_2CHCH_2MgCl}$ = 0.02, 0.10, 0.50, and 1.00 referenced to CH_3-Si(111) used to quantify mixed monolayer composition. The C=C stretch of the allyl-group at 1628 cm^{-1}, the CH_3- umbrella mode at 1257 cm^{-1}, and the CH_3- γ mode at 754 cm^{-1} are all visible. b) Magnification of 1628 C=C stretching mode. c) A combination of factors, including interference in the IR spectra caused by slight differences in Si wafer thickness, limited the precision with which the weak signals of interest allowed for a quantitative determination of the monolayer-

composition. Hence the composition of the MM-Si(111) surfaces was qualitatively compared to that of CH_3-Si(111) and CH_2CHCH_2-Si(111) using TIR spectroscopy. The fractional coverage of methyl groups, $\theta_{Si\text{-}CH_3}$ = (peak intensity of MM-Si(111))/(peak intensity of CH_3-Si(111)), was determined by the half-peak areas of the 1257 cm^{-1} (CH_3 umbrella) and 754 cm^{-1} (CH_3 γ) vibrational modes of MM-Si(111) surfaces. The fractional coverage of allyl groups, $\theta_{Si\text{-}CH_2CHCH_2}$ = 0.8*(peak intensity of MM-Si(111))/(peak intensity of CH_2CHCH_2-Si(111)), was determined using the 1628 cm^{-1} (C=C) peak area, where 0.8 is the fractional Si-C coverage of CH_2CHCH_2-Si(111) surfaces as determined by XPS. The error bars indicate ± 1 standard deviation. Figure S2.c shows that CH_3- and CH_2CHCH_2- groups were both present on the surface, and that the MM-Si(111) monolayer compositions were not linearly dependent on the compositon of the reaction solution.

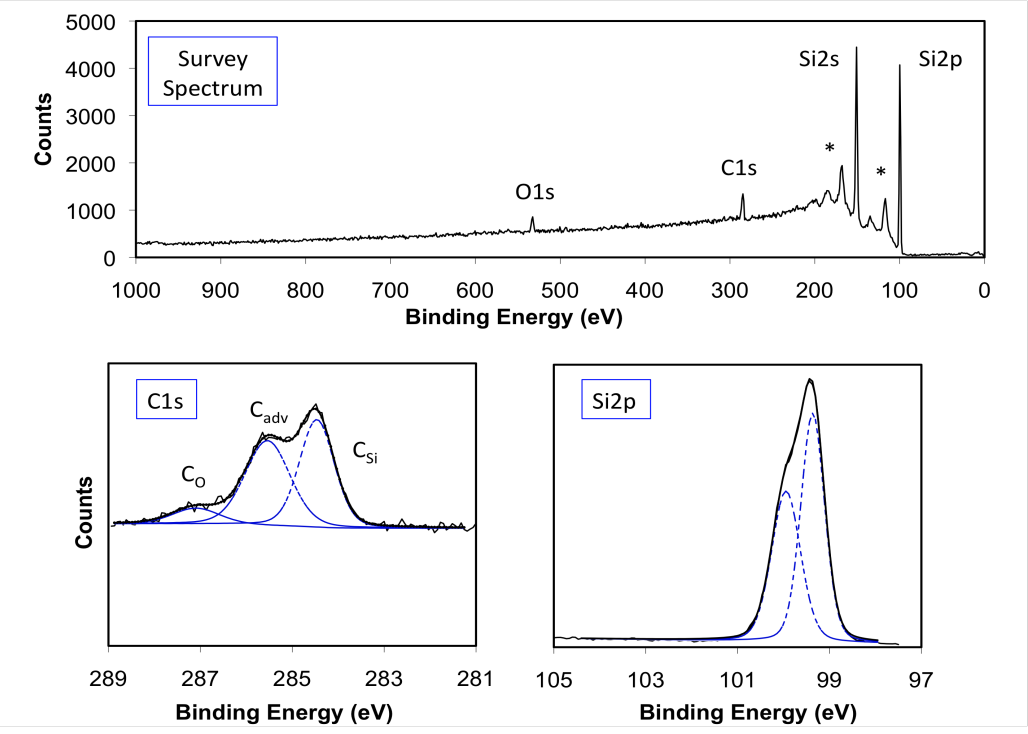

Figure S3. Typical XPS spectrum of CH_3-Si(111) showing survey spectrum and high reslution Si2p and C1s (2.5x scans of Si) regions. Peaks were fit using a Shirley background. C region was fit to C-O, adventitious C, and C-Si. Si region was fit to bulk Si, with no observed SiO_x for any CH_3-Si(111), MM-Si(111), or CH_2CHCH_2-Si(111) within the resolution of the instrument. *Si shake-down modes.

II. XPS-data workup

Oxide coverages were determined by integration of the area under the broad oxygen-shifted Si 2p peak centered around 102.5 binding eV. This peak was comprised of SiO_2 and suboxides. This peak area was ratioed to the area of the bulk Si $2p_{3/2}$ and $2p_{1/2}$ peaks. Using ESCA 2000 Anaylsis Application v2.01.01 integration software, the peak shapes were fitted to Voigt function fixed at 95% Gaussian and 5% Lorentzian line shapes. The fractional monolayer coverage of oxide species on the surface was determined using the substrate-overlayer model (Seah, M. P. In *Practical surface Analysis*, 2nd ed.; Briggs, D; Seah, M. P., Eds.; John Wiley Sons: Chichester, 1990; Vol. 1, pp 201-255.):

$$\frac{d_o}{d_1} = \lambda_o \sin\theta \left\{ \ln\left[1 + \left(\frac{I_{Si}^{\,0}}{I_o^{\,0}} \right) \left(\frac{I_o}{I_{Si}} \right) \right] \right\}$$

where d_o is the overlayer thickness, d_1 is the thickness of monolayer of oxide (3.5 Å), and l_o is the attenuation factor of the oxide layer (26 Å). q is the takeoff angle for the measurement (35°), $I_{Si}^{\,0}/I_o^{\,0}$ is a normalizing factor for the particular instrument used (1.3 for this instrument, Webb, L. J.; Lewis, N. S. *J. Phys. Chem. B.* **2003**, *107*, 5404-5412.), and I_{Si}/I_o is the ratio of the peak area of the oxide-shifted silicon to the area of the unshifted silicon peak.

Data from the high resolution carbon 1s emission region were fitted to three peaks, representing a higher binding energy peak of oxygen bonded carbon ~286.9 eV, a carbon bonded to carbon peak at ~285.0 eV, and a low binding energy peak of silicon bonded to carbon at ~284.3 eV. The peaks were allowed to float, though the full width at half max (fwhm) was fixed at 0.8 eV for silicon bonded to carbon. The C=C character in the carbon bonded to carbon peak caused a shift in that peak position among the various MM-Si surfaces, so a fixed separation between the carbon bonded to carbon and silicon bonded to carbon peaks was not imposed. The area of the silicon bonded to carbon peak was ratioed to the bulk Si $2p_{3/2}$ and Si $2p_{1/2}$ peaks to normalize for instrument focus. This ratio was then compared among the surfaces. The CH_3-Si(111) surface was used as a $\theta_{Si\text{-}C} = 1.00$ reference, so $\theta_{Si\text{-}C}$ for each MM-Si(111) surface was calculated as $(C_{Si}/Si)_{MM\text{-}Si(111)}/(C_{Si}/Si)_{CH3\text{-}Si(111)}$.

III. Statistical analysis of XPS data

To determine whether the coverage of mixed-monolayer surfaces prepared using different fractions of CH_3MgCl and CH_2CHCH_2MgCl were statistically different, the confidence interval for the difference of expectations, assuming a normal distribution, was calculated. If the confidence interval does not include 0 (zero), they are, to 95 % certainty, different. If the confidence interval does include 0, they are not different. The confidence interval was calculated as follows:

$$\mu_1 - \mu_2 = \overline{x_1} - \overline{x_2} \pm ks$$

where μ is the expectation value, $\overline{x}$ is the mean, k is a tabulated value dependent on the sample-size, n is the sample-size, and s^2 is the pooled variance:

$$s^2 = ((n_1 - 1)s_1^2 + (n_2 - 1)s_2^2)/(n_1 + n_2 - 2)$$

All tables and formulas were obtained from: Raade, L; and Westergren, B; "Mathematics Handbook for Science and Engineering"; 1995; studentlitteratur; Lund; Sweden